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Counting Atoms in Giant Inorganic Molecules using EXAFS

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Recent progress in synthesis of "giant" polyoxomolybdate (POM) molecules [1,2] that are hypothesized to have a structure of hollow spheres or wheels and size of several nanometers in diameter has emphasized the need in their accurate structural characterization. Complementary to other techniques that characterize the size and mass of these molecules, EXAFS enables accurate determination of the number of different units (Fig. 1) in the molecule, thus allowing to obtain the number of atoms and to choose between alternative models of atomic packing in the molecules. We developed a computer program to calculate the EXAFS pair distribution functions (PDF) for Mo-O and Mo-Mo neighbors in an arbitrary cluster of atoms. Using the crystallography data for the "small" sphere molecules [$Mo_{132}O_{372}(HCOO)_{30}$], or Mo132 (Fig. 2), its PDFs were obtained to be in an excellent agreement with the coordination numbers, distances and their enhanced (due to the configurational disorder) σ^2 measured in the EXAFS experiment (Fig. 3). The EXAFS measurements of the recently synthesized [2] "big" molecules were analyzed following the same procedure and, among other new results, the decrease in the relative number of Mo(V)-Mo(V) bonds to the number of other Mo-Mo bonds was obtained, compared to that in Mo132. This indicated that the "big" POM had higher percentage of Mo(VI) than Mo132 which was proved quantitatively by other experiments.

References:

1. Inorg. Chemistry home page at the University of Bielefeld: http://chexray4.uni-bielefeld.de/
2. T. Liu, Science Highlights, NSLS, Brookhaven National Laboratory, Upton, NY, 2002.

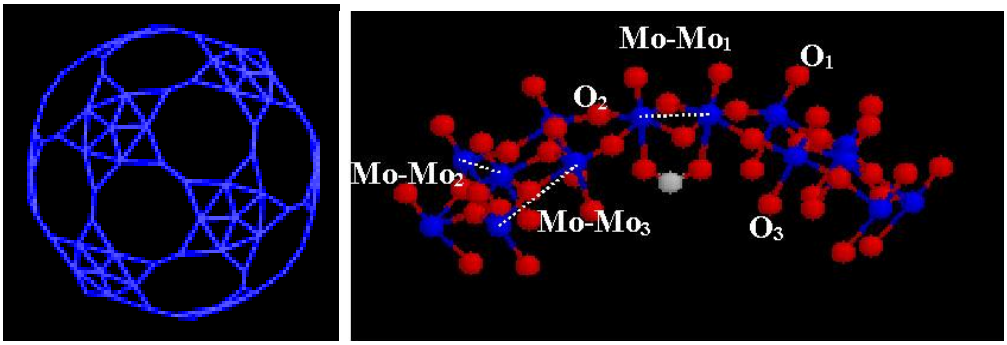

Figure 1. Molybdenum frame (left) and a symmetry element containing two Mo pentagons and the Mo-Mo bridge (right) in a [Mo_{132} O_{372} $(HCOO)_{30}$] molecule [1]. Shown also are different types of Mo-O and Mo-Mo pairs, and different types of O atoms.

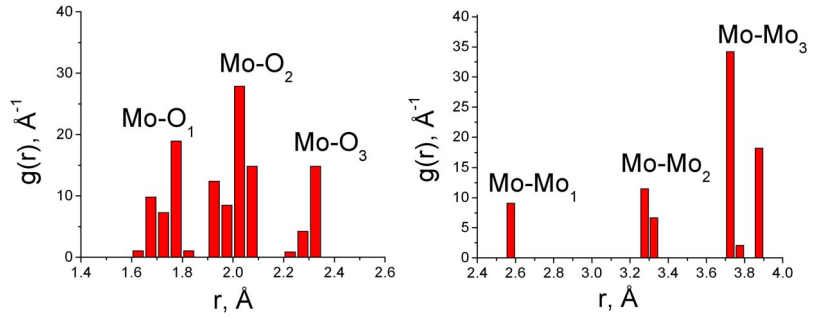

Figure 2. Average (per Mo atom) Mo-O (left) and Mo-Mo (right) pair distribution functions calculated for the [Mo_{132} O_{372} $(HCOO)_{30}$] structure (Fig. 1)

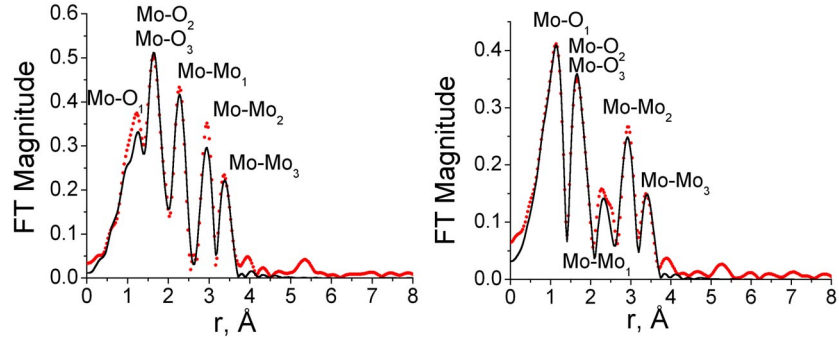

Figure 3. Fourier Transforms of the EXAFS data (symbols) and theoretical fit (solid), uncorrected for the photoelectron phase shifts, for the "small" ([Mo_{132} O_{372} $(HCOO)_{30}$], left) and the "big" spheres (right).